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Simultaneous pretreatment and acidogenesis of solid food wastes by a  
rotational drum fermentation system with methanogenic leachate  
recirculation and andesite porphyry addition

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## 1    **Abstract**

2        A simultaneous pretreatment and acidogenesis process was developed by  
3    recirculating methanogenic leachate and adding andesite porphyry (WRS) powder to a  
4    rotational drum fermentation system to enhance the anaerobic digestion of solid food  
5    wastes. In the continuous operations, methanogenic leachate recirculation  
6    significantly increased hydrolysis rates and volatile solids (VS) degradation. The VS  
7    degradation ratio and the hydrolysis rate constant at a higher leachate recirculation  
8    ratio (2:1 weight ratio of methanogenic leachate to substrate) were increased by 2.1-  
9    and 1.4-fold, respectively, compared to those of the lower ratio (1:1 leachate  
10    recirculation ratio). A 10% (weight ratio of WRS to substrate solid content) WRS  
11    addition assisted the biochemical reactions in the process at the higher leachate  
12    recirculation ratio was employed. The hydrolysis rate constant and VS degradation  
13    were elevated by 54.7% and 63.9%, respectively, with the WRS addition. Besides, the  
14    WRS addition enhanced the VA formation and its conversion to biogas.

## 15   **Highlights**

- 16    •    A simultaneous pretreatment and acidogenesis process for solid wastes was  
17        developed.
- 18    •    The methanogenic leachate considerably enhanced the hydrolysis of solid food  
19        wastes.

- 1 • The biochemical reactions significantly happened due to the mineral clay  
2 addition.

3 ***Key words:***

4 Leachate recirculation, andesite porphyry, simultaneous pretreatment and  
5 acidogenesis, solid food waste, rotational drum fermentation system

6

## 1. Introduction

Bioenergy from solid organic wastes is an excellent alternative to traditional fossil fuels when considering greenhouse gas emission control. Solid food wastes, comprising large fractions of municipal solid wastes, are amenable to bioenergy recovery by anaerobic conversion due to their large biodegradable fractions and moisture. The anaerobic conversion of solid food wastes to the end products CH<sub>4</sub> and CO<sub>2</sub> proceeds in a series of complex biochemical steps due to the lignin content of the solid food wastes (Converti et al., 1999). Hydrolysis is the rate-limiting step in the overall anaerobic conversion of solid substrates (Fdez-Guelfo et al., 2011). The hydrolysis rate mainly depends on the biodegradability of the substrate and the availability of microbes/enzymes (Veeken and Hamelers, 1999), and influenced by many other factors such as rheological properties (Kedziora et al., 2006).

Pretreatments by mechanical, chemical, thermal and combined treatments have been used for decades in the food industry and for biofuel production. Pretreatment contributes to both the reduction of particle size and the rearranging/breaking of some chemical bonds (McIntosh and Vancov, 2011; Seehra et al., 2012). Ball milling is traditionally applied as a mechanical pretreatment for its ability to rapidly reduce particle sizes and m Among the different ball milling pretreatments, wet milling is preferred to dry milling due to the higher pulverization efficiency (Charkhi et al., 2010) and lower energy consumption (Fuerstenau and Abouzeid, 2002) of wet ball

1 [milling](#). In the wet ball milling process, the pulverization is usually enhanced by  
2 increasing the moisture of the feedstock or by adding extra water ([Fuerstenau and](#)  
3 [Abouzeid, 2002](#)). Wet ball milling also meets the requirements for pretreating solid  
4 food wastes for anaerobic digestion.

5 In the anaerobic digestion process, the addition of a methanogenic process  
6 leachate instead of extra water during the wet ball milling process is conducive to  
7 water conservation ([Shahriari et al., 2012](#)). Using leachate recirculation to enhance the  
8 anaerobic digestion of solid food wastes ([Chen et al., 2008](#)) resulted in a similar VA  
9 yield (0.13 g-VA/g-VS) to that (0.11 g-VA/g-VS) of water flushing ([Gan et al., 2008](#)).  
10 Leachate recirculation improves the rheological properties of substrates and supplies  
11 enzymes and microbes to the pretreatment process. The enzymes and microbes also  
12 biochemically pretreat the solid substrates. Recycled leachate lowers the acidogenic  
13 product concentrations and buffers its inhibition to the hydrolysis and acidogenesis  
14 processes as the biochemical pretreatment occurs ([Sponza and Agdag, 2004](#)).  
15 Pretreatment using leachate recirculation ([Zhang et al., 2009](#)) and wet ball milling has  
16 been reviewed recently ([Chen et al., 2007](#)).

17 Although wet ball milling with leachate recirculation enforces the stabilization of  
18 food waste, the acidogenic products are prone to accumulation when low recirculation  
19 ratios are used. The accumulated acidogenic products caused the pH decrease and the  
20 increase of unionized volatile acid (UVA) . The extremely low pH and UVA inhibited  
21 the activity of methanogens and acidogens and may even lead to a failure of the entire

1 anaerobic process (Wang et al., 1999). Many experimental efforts have aimed to  
2 alleviate this inhibition, including lowering the product concentrations (Gan et al.,  
3 2008), electrodialysis (Yi et al., 2008), pervaporation (Cui et al., 2004) and removal of  
4 the products in situ (Cheng et al., 2010). Adsorptions by porous media such as zeolite  
5 (Wang et al., 2011), activated carbon (Pyrzynska and Bystrzejewski, 2010) and resin  
6 (Lin and Juang, 2009) are an interesting method for in-situ removal. In recent years,  
7 andesite porphyry (known as wheat-rice-stone, WRS, in Asia), a kind of natural clay  
8 mineral, has been applied as a candidate to remove the acidogenic products in situ and  
9 thereby assist hydrolysis and acidogenesis (Cheng et al., 2010). WRS not only  
10 adsorbs the accumulated acidogenic products due to its unique tetrahedral structure  
11 with micro- and nano-channels, but also dissociates and releases cations, including  
12  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Na}^{+}$ , during the acidogenesis of solid food wastes (Li et al., 2009;  
13 Cheng et al., 2010). The dissociated cations provide nutrition required by the  
14 microbes (Cheng et al., 2010). The acidogenic product adsorption and cation  
15 dissociation contribute positively to the anaerobic digestion of solid food wastes.

16 In this study, a rotational drum fermentation (RDF) system with methanogenic  
17 leachate recirculation has been developed. The objectives of the work were to (1)  
18 pretreat and simultaneously acidify solid food wastes as part of anaerobic digestion by  
19 an RDF system with methanogenic leachate recirculation and (2) enhance  
20 pretreatment and acidogenesis of solid food wastes by methanogenic leachate  
21 recirculation and WRS addition.

## 1    **2. Materials and methods**

### 2    *2.1. Materials*

#### 3    *2.1.1 Substrate and seeding sludge*

4        Fresh soybean meal (approximately 24.1% total solids, TS) was collected from a  
5    dining hall of the China Agricultural University (Beijing, China) to be used as the  
6    substrate. The composition of the dry soybean meal was as follows: protein (22.6%),  
7    lipid (19.6%), sugar (37.0%), cellulose (14.5%), ash (6.1%) and other constituents  
8    (0.2%). The initial mean particle size of the raw material was 673  $\mu\text{m}$ .

9        Anaerobic digestion sludge was taken from a municipal wastewater treatment  
10   plant (Beijing, China) for use as the seeding sludge. The TS, VS and of the sludge  
11   were 2.6%, 1.4% and 7.8, respectively. The initial volatile fatty acids of the substrate  
12   and the sludge were 0 and 0.04 g/L, respectively.

#### 13   *2.2.2. Andesite porphyry*

14        Andesite porphyry (WRS) was collected from the Changping Mine (Beijing,  
15   China) for use as an additive during the hydrolysis and acidogenesis of the solid food  
16   wastes. The chemical composition of the WRS used was as in Li et al ([Li et al., 2009](#)).  
17   The WRS was washed 2-3 times with distilled water and then dried in an oven at 105  
18    $^{\circ}\text{C}$  to constant weight.



### 1    2.1.3. *Methanogenic leachate*

2        The methanogenic leachate was obtained from a sound mesophilic (35-37 °C)  
3    methanogenic process. The methanogenic process was fed daily with acetic acid and  
4    synthetic wastewater (Chang et al., 1982) and run well for over 2 years. The  
5    methanogenic effluent was centrifuged at 3000 rpm for 3 min, and the supernatant  
6    was recycled into the acidogenic process as the methanogenic leachate. The average  
7    pH of the leachate was 7.2.

### 8    2.2. *Experimental apparatus*

9        The RDF system developed by Jiang et al (Jiang et al., 2005) was employed to  
10    perform the simultaneous pretreatment and acidogenesis of the solid food wastes. The  
11    RDF system consisted of six drum fermentors, and each fermentor's working volume  
12    was 3.6 L. The mechanical pretreatment was mainly performed by rotating the  
13    fermentor with 26 aluminum oxide milling balls (diameter=30 mm), taking up 10% of  
14    each fermentor (in volume). Each fermentor was rotated automatically for 15 min  
15    every 45 min at 12 rpm and  $35 \pm 1$  °C during the experimental period.

### 16    2.3. *Experimental procedure*

#### 17    2.3.1. *Batch operation*

18        In batch operation, two fermentors, LB1 and LB2, were used to evaluate the effect  
19    of leachate recirculation on the simultaneous pretreatment and acidogenesis of solid

1 food wastes, while the other four fermentors, B11, B12, B21 and B22, were used to  
2 evaluate the effect of leachate recirculation with the addition of WRS. The seeding  
3 sludge was considered as the methanogenic leachate in the batch operation. The  
4 leachate recirculation ratio (the weight ratio of methanogenic leachate to substrate)  
5 was 1:1 for LB1, B11 and B12 and 2:1 for LB2, B21 and B22. Five percent WRS (the  
6 weight ratio of WRS to substrate solid content) was added to B11 and B21, and 10%  
7 to B12 and B22. The detailed feeding conditions were shown in Table 1

8 The batch operations lasted for 10 days. Samples were withdrawn for the analysis  
9 of pH, TS (total solids), TDS (total dissolved solids), VS (volatile solids), TVA (total  
10 volatile acids), volatile acids (VA) spectra, mean diameter (MD), cation concentration  
11 (CC) and ATP concentration on alternate days.

### 12 2.3.2. *Continuous operation*

13 Fermentors LC1, LC2, C11, C12, C21 and C22 were used for continuous  
14 operation. Their detailed feeding conditions are shown in Table 2.

### 15 **Table 2 Daily operation conditions for the continuous operation experiment**

16 The hydraulic retention time (HRT) of the continuous operation was 10 days. The  
17 continuous operation was maintained with daily feedings and withdrawals for at least  
18 3 HRTs before reaching pseudo-steady state. The pH was tested every day, while other  
19 parameters were measured on alternate days during the pseudo-steady state as for the  
20 batch operation.

## 2.4. Measurements and analyses

The pH, TS, TDS, VS and VA levels were measured using the sewage test procedure (APHA, 2005). MDs were measured using a laser particle size analyzer (LS230, COULTER). ATP concentrations, used to quantify the microbe populations, were determined using an ATP analyzer (AF-100, DKK-TOA). The sample was centrifuged at 6000 rpm for 5 min, and then the supernatant was filtered through a 0.45 µm membrane filter to assess VA spectra by a high-performance liquid chromatograph (LC-10AVP, SHIMADZU) with an Atlantic dC column (18.5µm, 4.6×150mm, WATERS) at 30 °C.

## 2.5. Parameter calculations for the degradation of anaerobic solid waste

### 2.5.1. Hydrolysis rate constant

The hydrolysis of a solid substrate can be represented by the surface based kinetics (SBK) model (Sanders et al, 2000). The hydrolysis rate constant can be expressed as follows:

$$K_{sbk} = \rho \frac{R_0 - R_t}{t} \quad (0)$$

where  $\rho$  (kg/m<sup>3</sup>) is the density of the substrate,  $R_0$  (m) is the mean size of the substrate particle at time 0, and  $R_t$  (m) is the mean size of the substrate particle at time t.

### 2.5.2. Total dissolved solids generated (TDS<sub>G</sub>)

The TDS<sub>G</sub> can be calculated using equation (2)

$$TDS_G = TDS_t - TDS_0 + VS_0 - VS_t \quad (0)$$

where  $TDS_t$  (g/L) and  $TDS_0$  (g/L) are the total dissolved solids at time t and time 0, respectively and  $VS_0$  (g/L) and  $VS_t$  (g/L) are the VS contents of the broth at time 0 and time t, respectively (Cheng et al., 2010).

### 2.5.3. Unionized VA concentration

UVA concentration can be determined using following equation:

$$UVA = VA \frac{10^{(pKa-pH)}}{1 + 10^{(pKa-pH)}} \quad (0)$$

where  $pKa$  is the dissociation constant of the acid in water; the  $pKa$  of acetic acid is 4.762 at 35 °C (Weast, 1981).

### 2.5.4. Specific growth rates of $TDS_G$ , VA, and ATP

The specific growth rates of ATP or the other parameters can be calculated using equation (4):

$$\mu = \frac{1}{t} \ln(X_t/X_{t-1}) \quad (0)$$

where  $\mu$  ( $d^{-1}$ ) is the specific growth rate of  $TDS_G$ , VA or ATP;  $X_t$  is the value of  $TDS_G$ , VA or ATP at time t;  $X_{t-1}$  is the value of  $TDS_G$ , VA or ATP at time t-1 and t is the sampling interval.

### 2.5.5. VS degradation ratio ( $R_{VS}$ )

The  $R_{VS}$  can be calculated using equation (5):

$$R_{vs} = \frac{VS_0 - VS_t}{VS_0} \times 100 \quad (0)$$

where  $R_{VS}$  (%) is the VS degradation ratio;  $VS_0$  (g/L) is the initial concentration and  $VS_t$  (g/L) is the concentration of a sample taken from the fermentor at time t.

#### 2.5.6. Particle size distribution

The particle size distribution is characterized by the MD and the relative span ( $S_L$ ) (Igathinathane et al., 2009; Resch et al., 2011). The relative span is determined using equation (6):

$$S_L = \frac{D_{90} - D_{10}}{D_{50}} \quad (0)$$

where  $S_L$  is the relative span;  $D_{10}$ ,  $D_{50}$  and  $D_{90}$  are the diameters as the cumulative volumes reached 10%, 50% and 90%, respectively.

#### 2.5.7. VA yield

The VA yield is expressed by the equation as follow:

$$\eta = \frac{VA_t - VA_0}{VS_0 - VS_t} \quad (1)$$

where  $VA_t$  (g/L) and  $VA_0$  (g/L) are the VA concentration of the sample at time t and time 0, respectively;  $VS_0$  (g/L) is the initial concentration and  $VS_t$  (g/L) is the concentration of a sample taken from the fermentor at time t.

### 3. Results and discussion

#### 3.1. Effect of leachate recirculation on simultaneous pretreatment and acidogenesis of solid food wastes

##### 3.1.1 Batch operation

The PSDs of broths in LB1 and LB2 are shown in Fig.1 (a and b). The curve of the particle size distribution changed from one dominated by large particles to one dominated by smaller ones (from right to left in the figure) over the operation time. The  $S_L$ s obtained using equation (0) for LB1 and LB2 peaked at 2.70 and 3.16, respectively, much higher than that of the original feedstock (1.53). The increases in  $S_L$  suggest that substrate flocs were ground into finer particles. The calculated MDs of substrate particles in the batch operations are shown in Fig. 2 (a). The MDs decreased linearly in LB1 and LB2 from 673 to 567 and 96  $\mu\text{m}$ , respectively. According to the linear regression of Fig. 2 and equation (0), the calculated  $K_{sbk}$  values for LB1 and LB2 were 11.4 and  $50.0 \times 10^{-3} \text{ kg m}^{-2} \text{ d}^{-1}$ , respectively. The  $K_{sbk}$  of LB2 was 4.4-fold higher than that of LB1. The dramatically higher  $K_{sbk}$  of LB2 was ascribed to the higher humidity that resulted from the increased leachate recirculation ratio. The higher humidity reinforced the impact of the milling balls onto the substrate flocs, the dispersion of flocs and the shear flow in the rheology (Izumi et al., 2010). Both the higher impact and higher shear flow enhanced splitting of the substrate agglomerates and broke crystal structures.

**Fig. 1 Particle size distributions in the batch operations**

**Fig. 2 Time courses for particle MDs in the batch experiments**

Enrichment with the enzymes and microbes in the leachate caused biodegradation occur during the mechanical pretreatment. The VS degradation rate was determined using a regression (Fig. 3 (a)). The VS degradation rates for LB1 and LB2 were 6.2 and 4.5 g L<sup>-1</sup> d<sup>-1</sup>, respectively. The TDS<sub>G</sub> grew logarithmically during the batch operation. The specific growth rate of the TDS<sub>G</sub> ( $\mu_{\text{TDSG}}$ ) was calculated using equation (0) as 0.16 and 0.17 d<sup>-1</sup> for LB1 and LB2, respectively. The higher TDS<sub>G</sub> and the VS degradation rate in LB1 were caused by the lower leachate recirculation ratio. Similar results were obtained by Zhou et al (Zhou et al., 2011). In the lower leachate recirculation ratio fermentor (LC1), the presence of more readily biodegradable substrate (the initial total dissolved solids TDS<sub>0</sub>, 14.0 g/L) ensured the anaerobes' growth during the initial period.

**Fig. 3 Time courses for TDSG and VS contents**

The specific growth rates of the anaerobes (represented by the ATP concentration  $\mu_{\text{ATP}}$  (APHA, 2005) in LB1 and LB2 were 5.40 and 5.04 d<sup>-1</sup>, respectively. The growth of the anaerobes not only accelerated VS degradation, but also enhanced the formation of VAs. The specific growth rates ( $\mu_{\text{VAS}}$ ) for the TVAs in LB1 and LB2 were similar, with values of 0.29 and 0.28 d<sup>-1</sup>, respectively. The yields of VA and ionized VA (IVA) for LB1 and LB2 tended similar to the  $\mu_{\text{VAS}}$ . The VA yields for LB1

1 and LB2 were 0.16 and 0.15 g-VA/g-VS, respectively. The IVA ratio of LB2 was  
2 higher than that of LB1 during the batch operation, despite the finding that the IVAs  
3 for both LB1 and LB2 were no more than 30% of the TVAs. Apparently, more  
4 leachate recirculation had a greater effect on the mechanical than the biochemical  
5 aspect of the in this work.

### 6 *3.1.2. Continuous operation*

#### 7 **Fig. 4 Particle size distributions in the continuous operations**

8 The parameters in the continuous operation trials were obtained by averaging the  
9 data obtained under steady state. The particle size distributions of LC1 and LC2 are  
10 shown in Fig. 4. The particles spanned broader ranges in LC1 and LC2 than in the  
11 feedstock. The  $S_L$ s of LC1 and LC2 were higher by 31.9% and 35.2% than that of the  
12 feedstock (1.53), respectively. The higher  $S_L$  of LC2 indicated that substrates were  
13 ground into finer particles in this fermentor. The pretreatment characteristics of the  
14 continuous operations are summarized in Table 3. The MDs for LC1 and LC2 were  
15 reduced from 744  $\mu\text{m}$  in the feedstock to 662 and 491  $\mu\text{m}$ , respectively. The  
16 calculated  $K_{sbk}$  of LC2 was higher by 2.1-fold than that of LC1. Higher  $K_{sbk}$  and lower  
17 MD were obtained at the higher moisture content (LC2), which coincided with the  
18 results in the batch operation. The substrate particles were stressed mechanically by  
19 the compression, impact and the friction of the milling balls in this work. The  
20 breakage of substrate particles depended on the yield stress of itself and the stressing



1 intensity. The yield stress dropped at certain higher moisture content (Müller et al.,  
2 2013), meaning particles were apt to be broken mechanically. In addition, the particles  
3 were softened in the structure, thus the accessibility of the substrate was enhanced.  
4 This was evidenced by the results and  $R_{VS}$  and  $TDS_G$ .

5 The  $R_{VS}$  of LC2 was 2.4-fold higher than that of LC1. Similar to the VS  
6 degradation, the  $TDS_G$  for LC2 was more than 2-fold greater than that of LC1. The  
7 finer particles presented larger surface area, and available for the microorganisms,  
8 resulting a higher  $R_{VS}$  and  $TDS_G$ . The solubility of substrate were also enhanced by  
9 the wet ball milling pretreatment (Izumi et al., 2010). In another word, these favorable  
10  $TDS_G$ s were generated by the combination of mechanical pretreatment with  
11 biochemical reactions.

12 **Table 3 Pretreatment characteristics of the continuous operations under steady**  
13 **state**

14 As shown in Table 4, the apparent VA yield of LC1 was 2.5-fold above that of  
15 LC2 despite their similar TVAs. The IVAs predominated in both LC1 and LC2. The  
16 IVA values were elevated significantly compared to those under continuous operation  
17 without leachate recirculation (Chen et al., 2008). The higher IVAs favored higher  
18 rates of methanogenesis.

19 The VA spectra appeared to be influenced by the leachate recirculation. The acetic  
20 acid contents of LC1 and LC2 were 31.1% and 14.6%, respectively, while the  
21 propionic acid contents were 20.7% and 36.5%, respectively. The ratio of propionic

1 acid to acetic acid (P/A) of LC2 greater than 1.4 or the was possibly considered as an  
2 indicator of failure (Hill et al., 1987), however, the lower amount of acetic acid in  
3 LC2 was caused by its conversion to biogas (methane and carbon dioxide) in this  
4 work. The biogas emission was observed during daily operations, during which 70%  
5 methane was generated from acetic acid. On the contrary, little biogas was observed  
6 in LC1. The rich leachate in LC2 introduced more microbes and enzymes and favored  
7 degradation of the acetate.

8 **Table 4 Acidogenesis characteristics of the continuous operations under steady**  
9 **state**

10 *3.2. Effects of leachate recirculation and WRS addition on simultaneous pretreatment*  
11 *and acidogenesis of solid food wastes*

12 *3.2.1. Batch operation*

13 Time courses for particle size distributions during the batch operations are shown  
14 in Fig. 1 (c-f). The calculated  $S_L$ s for B11, B12, B21 and B22 were 3.0, 2.49, 3.44 and  
15 2.98, respectively. The  $S_L$  for each run increased over the course of the reaction. The  
16 time courses for MDs during batch operation are shown in Fig. 2 (b). The MDs for  
17 B11, B12, B21 and B22 were 494, 294, 158 and 61  $\mu\text{m}$ , respectively. The MDs for  
18 B11 and B12 were lower by 12.8% and 48.1% than that of LB1, respectively. The MD  
19 for B21 was higher than that of LB2, while the MD for B22 was 63.5% of LB2's.  
20 Correspondingly, the  $K_{sbk}$ s obtained for B11 and B12 were 16.0 and 29.8  $\times 10^{-3}$  kg

1  $\text{m}^{-2} \text{d}^{-1}$ , and  $50.0$  and  $65.0 \times 10^{-3} \text{ kg m}^{-2} \text{d}^{-1}$  for B21 and B22, respectively. The  $K_{\text{sbk}}$   
2 for B11 and B12 were 1.4 and 2.6-fold higher than that of LB1 respectively. The  $K_{\text{sbk}}$   
3 for B21 was close to that of LB2 ( $50.0 \times 10^{-3} \text{ kg m}^{-2} \text{d}^{-1}$ ), while the  $K_{\text{sbk}}$  for B22 was  
4 1.3-fold higher than that of LB2. Compared to LB1 and LB2, the WRS addition  
5 significantly enhanced the substrate particle size reduction (except B21). Moreover,  
6 the WRS addition led to a faster substrate particle size reduction in the case of the  
7 higher leachate recirculation ratio. The WRS particles were much harder than the  
8 substrate particles. The elasticities of the WRS and substrate mixtures were lower than  
9 that of the substrate alone. With WRS addition, the substrate particles were more  
10 easily broken when they were impacted by the milling balls. In addition, the large  
11 amounts of cations such as  $\text{Ca}^{2+}$ ,  $\text{Na}^{+}$  and  $\text{Al}^{3+}$  in the WRS are prone to dissociation  
12 and formation of compounds such as  $\text{CaCl}_2$  and  $\text{CH}_3\text{COONa}$  in acidic broth. In the  
13 experiment, the compounds may have arranged their dipoles to reduce the flocs'  
14 surface energies and thereby aided the fragmentation of the solid substrates.

15 The time course of VS degradation and  $\text{TDS}_G$  is shown in Fig. 3. The VS  
16 degradation rates for B11, B12, B21 and B22 were  $7.0$ ,  $6.5$ ,  $4.6$  and  $5.5 \text{ g L}^{-1} \text{d}^{-1}$ ,  
17 respectively. The VS degradation rates for B11 and B12 were higher by 11.7% and 4.8%  
18 than that of LB1, respectively. The VS degradation rate for B21 was similar to that of  
19 LB2, while that of B22 was higher by 22.2% than that of LB2. The  $\text{TDS}_G$  grew  
20 logarithmically during the batch operation. The  $\mu_{\text{TDS}_G}$  for B11, B12, B21 and B22  
21 were  $0.15$ ,  $0.09$ ,  $0.07$  and  $0.13 \text{ d}^{-1}$ , respectively. Higher leachate recirculation and

1 more WRS addition were therefore favorable to the VS degradation.

2 The apparent VA yields for B11, B12, B21 and B22 were 0.09, 0.26, 0.16 and 0.31  
3 g-VA/g-VS, respectively. Compared to LB1 and LB2, more WRS addition favored  
4 more VA production (Li et al., 2009; Cheng et al., 2010). Formic acid predominated in  
5 fermentor B11 and B21, while succinic acid did in fermentor B12 and B22 during the  
6 initial period. Acetic acid predominated beginning on the 4<sup>th</sup> day in all the fermentors.  
7 The specific growth rates for acetic acid in B11, B12, B21 and B22 were 0.31, 0.30,  
8 0.24 and 0.31 d<sup>-1</sup>, respectively. The occupation of acetic acid was elevated by the  
9 WRS addition compared with LB1 and LB2. These results suggest that the WRS  
10 addition promoted the conversion of long-chain VAs to short ones. Among the short  
11 chain VAs, propionic acid is difficult to be converted to acetic acid by the  
12 microorganisms compared to butyric acid. On the contrary, acetic acid was prone to  
13 consumed by the methanogens. The higher acetic acid occupation implied a potential  
14 for the biogas production.

15 The data for VS degradation and VA production demonstrate that the WRS  
16 addition enhanced the biochemical reactions. These results were consistent with the  
17 anaerobes' growth as the  $\mu_{ATPS}$  for B11, B12, B21 and B22 increased by 5.9%, 24.5%,  
18 21.0% and 2.4% compared to LB1 and LB2.

### 19 3.2.2. Continuous operations

20 The parameters of the continuous operations were obtained by averaging data  
21 obtained under steady state. The particle size distributions are shown in Fig. 4.

1 Substrate particles smaller than 100  $\mu\text{m}$  were 5.7%, 11.7%, 16.4% and 32.6% of the  
2 totals, respectively, in comparison to those of LC1 (6.2%) and LC2 (8.7%). Aldin's  
3 work (Aldin, 2010) suggested that most biodegradable matter ranged from 0.001-100  
4  $\mu\text{m}$ . In our work, the WRS addition contributed to the conversion from raw materials  
5 to materials with high proportions of biodegradable constituents. The  $S_{LS}$  calculated  
6 using equation (0) for C11, C12, C21 and C22 were 1.99, 2.36, 2.64 and 3.02,  
7 respectively. The  $S_L$  of C11 was slightly lower than that of LC1, while the  $S_L$  of C12  
8 was higher by 16.8% than that of LC1. The  $S_{LS}$  of C21 and C22 were higher by 27.5%  
9 and 45.9% than that of LC2, respectively. These results suggest that more fine  
10 particles were produced due to the WRS addition.

11 Characteristics of the pretreatments are shown in Table 2. The MDs of fermentors  
12 C11, C12, C21 and C22 decreased from 673  $\mu\text{m}$  to 656, 628, 518 and 351  $\mu\text{m}$ ,  
13 respectively. The MDs of C11 and C12 were slightly lower than that of LC1. The MD  
14 of C21 was slightly higher than that of LC1, while the MD of C22 was lower by 39.8%  
15 than that of LC2. Correspondingly, the  $K_{sbk}$ s for C11 and C12 were higher by 7.3%  
16 and 41.5% than that of LC1, respectively. The  $K_{sbk}$  for C21 was close to that of LC2,  
17 while the  $K_{sbk}$  for C22 was higher by 54.7% than that of LC2. The higher leachate  
18 recirculation and WRS addition ratio led to the substrate particle shift from the large  
19 to the micro range.

20 The  $R_{VSS}$  and the  $TDS_G$ s are shown in Table 3. The  $R_{VSS}$  of C11 and C12 were  
21 close to that of LC1, whereas those of C21 and C22 were much higher than that of

1 LC2. The  $R_{VSS}$  of C21 and C22 were higher by 35.8% and 63.9% than that of LC2,  
2 respectively. The WRS was prone to dissociate cations, including  $Fe^{2+}/Fe^{3+}$ ,  $Ca^{2+}$  and  
3  $Mg^{2+}$ , and accelerated the oxidation/reduction reaction under the high leachate  
4 recirculation ratio. On the contrary, the WRS dissociation and cation transfers were  
5 perturbed in case of the lower leachate recirculation ratio. The leachate recirculation  
6 contributed 64.8% and 64.5% to the VS degradation, while WRS addition contributed  
7 35.2% and 35.5% to that in C11 and C12, respectively. The values for  $TDS_G$  showed  
8 similar trends to those for the VS degradation ratio. The highest  $TDS_G$  achieved was  
9 in C22, which was higher by 56.2% than that of LC2.

10 The TVA of C11 was higher by 8.7% than that of LC1, while the TVA of C12 was  
11 lower by 2.9% than that of LC1. The VA formation seemed to be little enhanced by  
12 WRS addition in the case of the lower leachate recirculation ratio, even though the  
13 TVAs for C21 and C22 were supposed to increase. Interestingly, the TVAs of C21 and  
14 C22 were lower by 14.4% and 28.8% than that of LC2, respectively. The decreased  
15 VAs were converted to biogas. In our work, biogas emission was observed in C21 and  
16 C22 during daily operations. The biogas emission should not only be ascribed to the  
17 reduction of particle size ([Zhang and Banks, 2013](#)), but also resulted from the WRS  
18 addition. As mentioned above, the cations dissociated from WRS had the enzyme and  
19 microorganisms sparked and promoted the acidogenesis and even the methanogenesis  
20 potentially.

21 Similar results were obtained for the distributions of the IVAs and UVAs and for

1 the VA spectra. The IVAs predominated in all the fermentors, which was possibly  
2 conducive to biogas formation. Compared to LC2, the acetic acid occupation  
3 decreased with the increased addition of WRS in C22. The decreased acetic acid was  
4 possibly converted to biogas. Notably, the occupation of propionic acid varied in the  
5 range of 29.2-58.5%. The TDSs were prone to conversion to propionate rather than to  
6 other VAs (such as butyrate, acetate and lactate) by lower energy demand during the  
7 biochemical reaction. However, propionate is more difficult to convert to acetate than  
8 to butyrate and lactate ([Azbar et al., 2001](#)).

#### 9 **4. Conclusion**

10 Methanogenic leachate recirculation and WRS addition were used to enhance  
11 pretreatment and acidogenesis of solid food wastes in batch and continuous operations.  
12 A higher leachate recirculation ratio from the methanogenesis to RDF system  
13 improved the mechanical pretreatment such as particle size reduction and TDS  
14 generation in anaerobic process. The 10% WRS addition at higher leachate  
15 recirculation ratio considerably enhanced the VS degradation, particle size reduction,  
16 VA formation and conversion to biogas.

#### 17 **Acknowledgements**

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19 Universities (2011JS121).

## 1 **Figure captions**

2 Fig. 1 Particle size distributions in the batch operations

3 Fig. 2 Time courses for particle MDs in the batch experiments

4 Fig. 3 Time courses for TDS<sub>G</sub> and VS contents

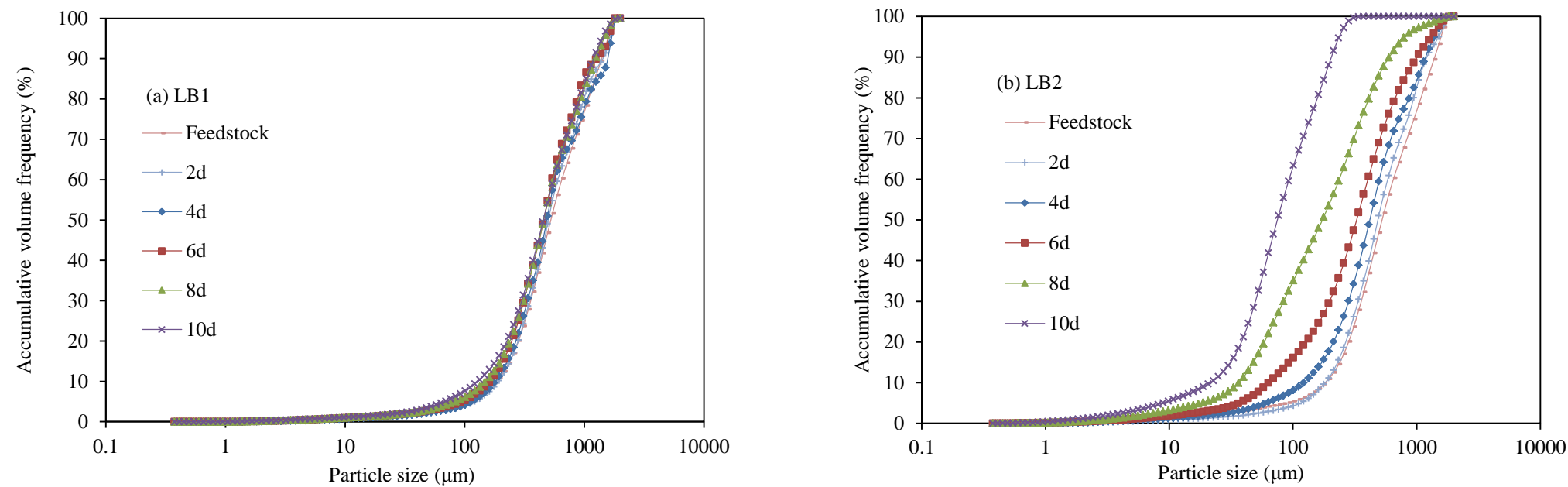
5 Fig. 4 Particle size distributions in the continuous operations

6

7



**Fig. 1**



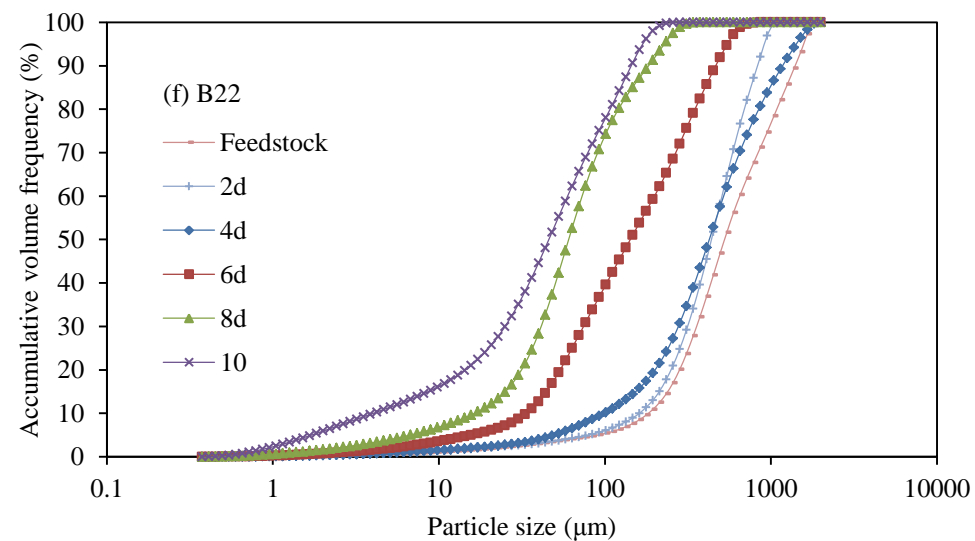
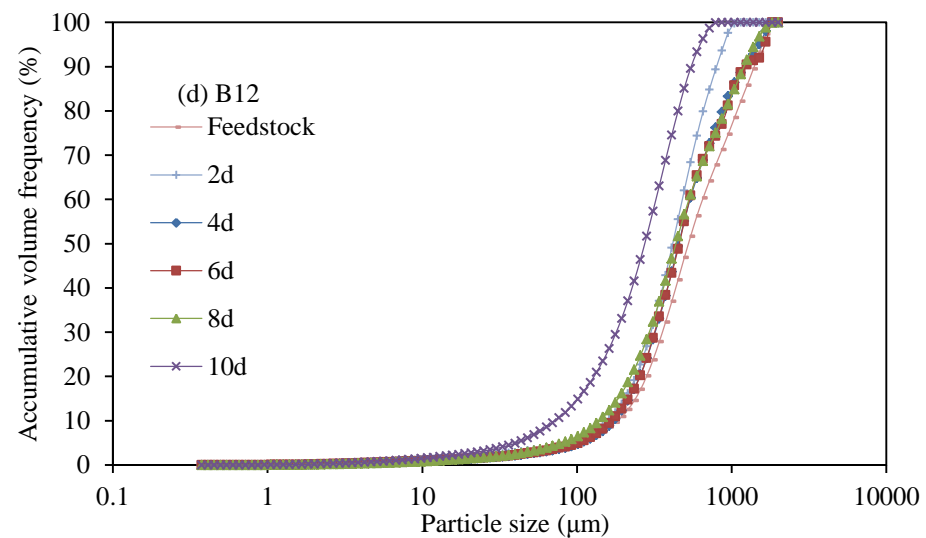
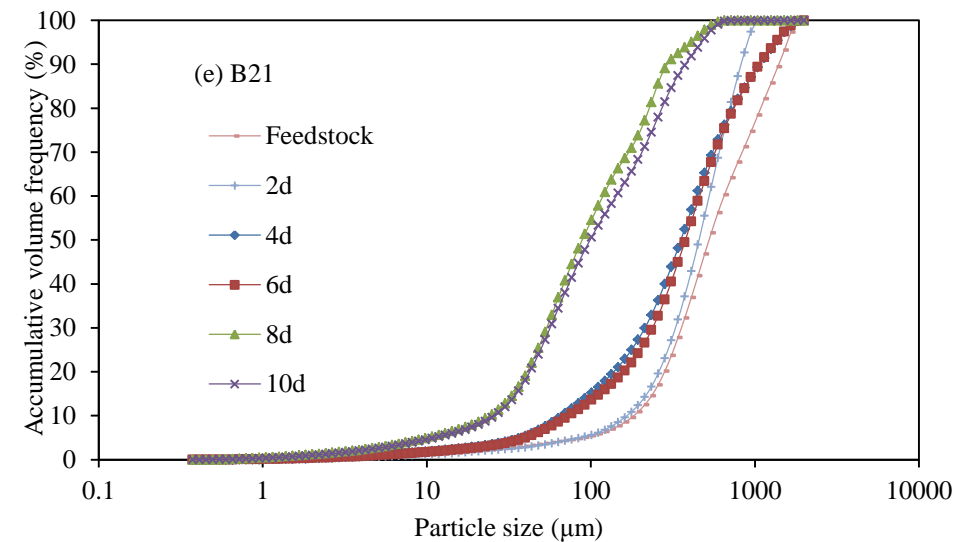
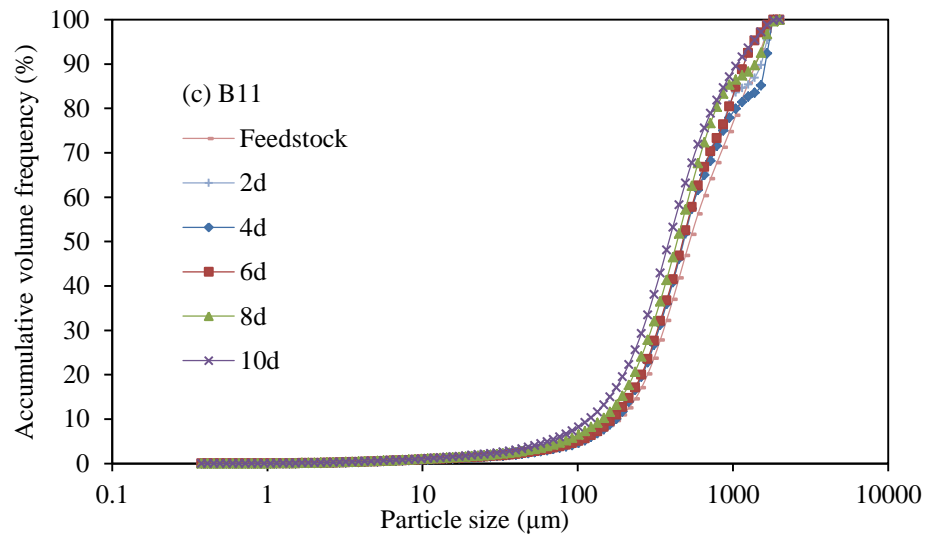


Fig. 1 Particle size distributions in the batch operations

**Fig. 2**

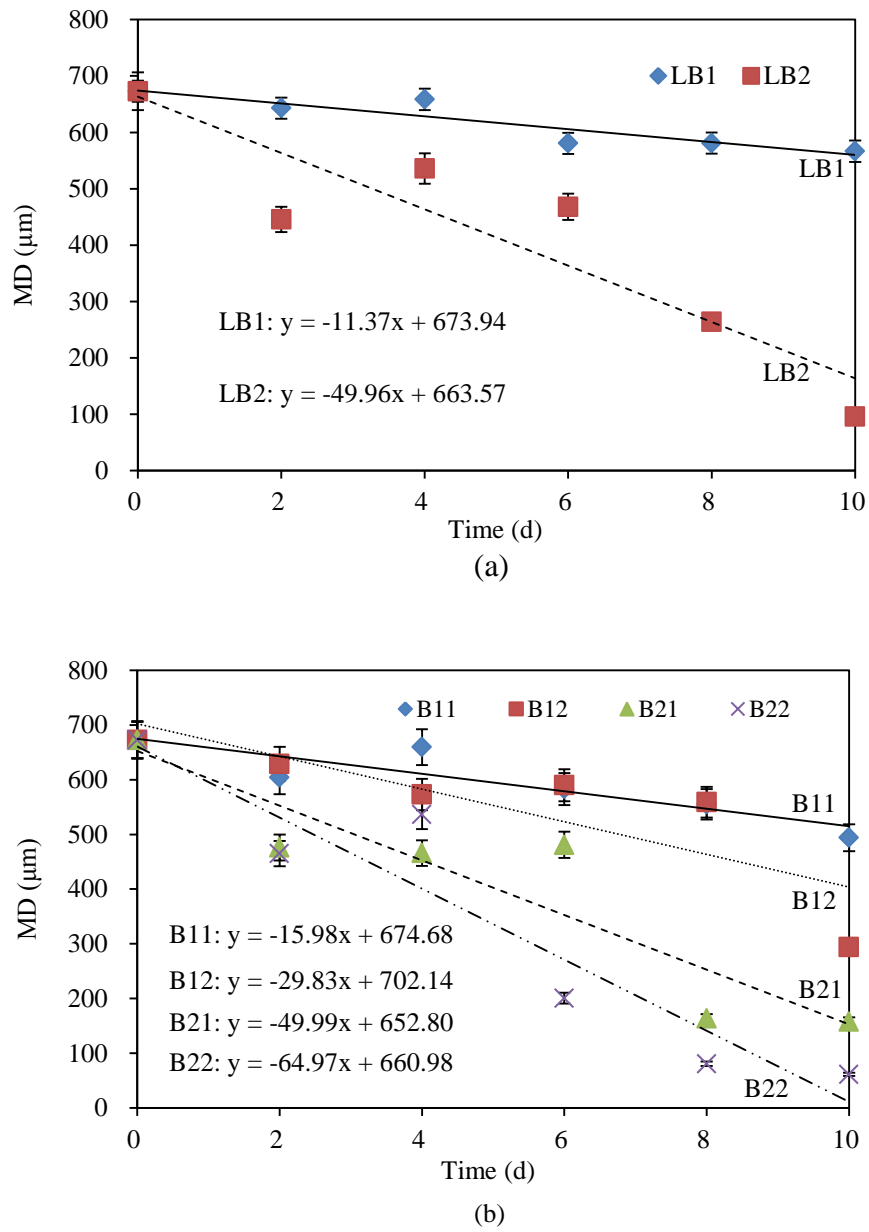


Fig. 2 Time courses for particle MDs in the batch experiments

**Fig. 3**

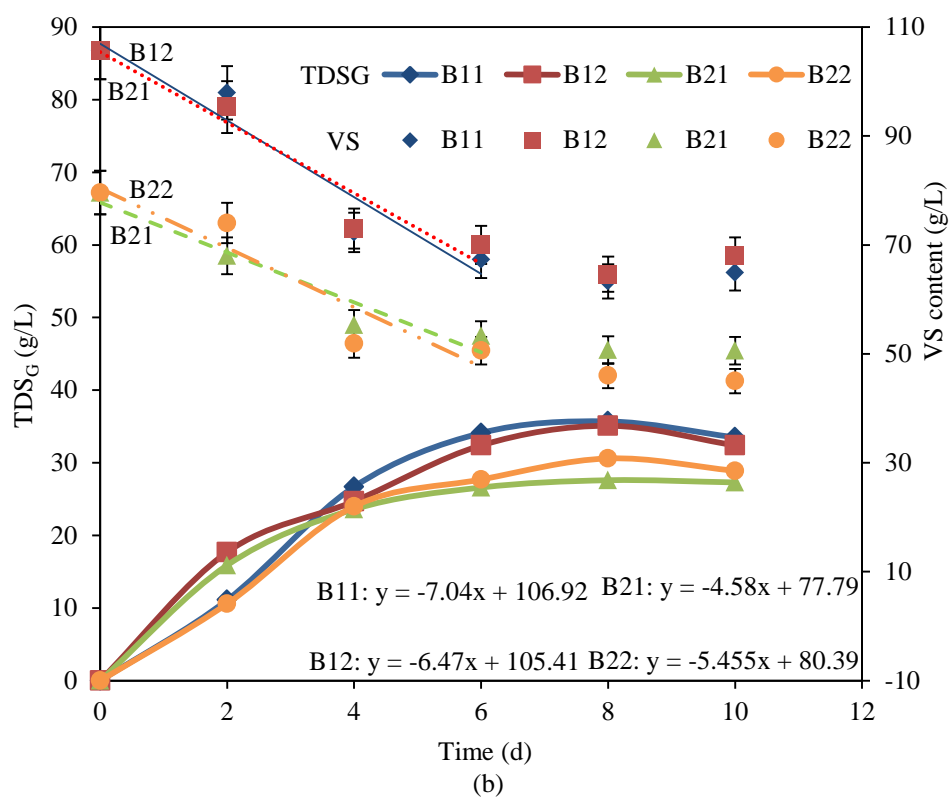
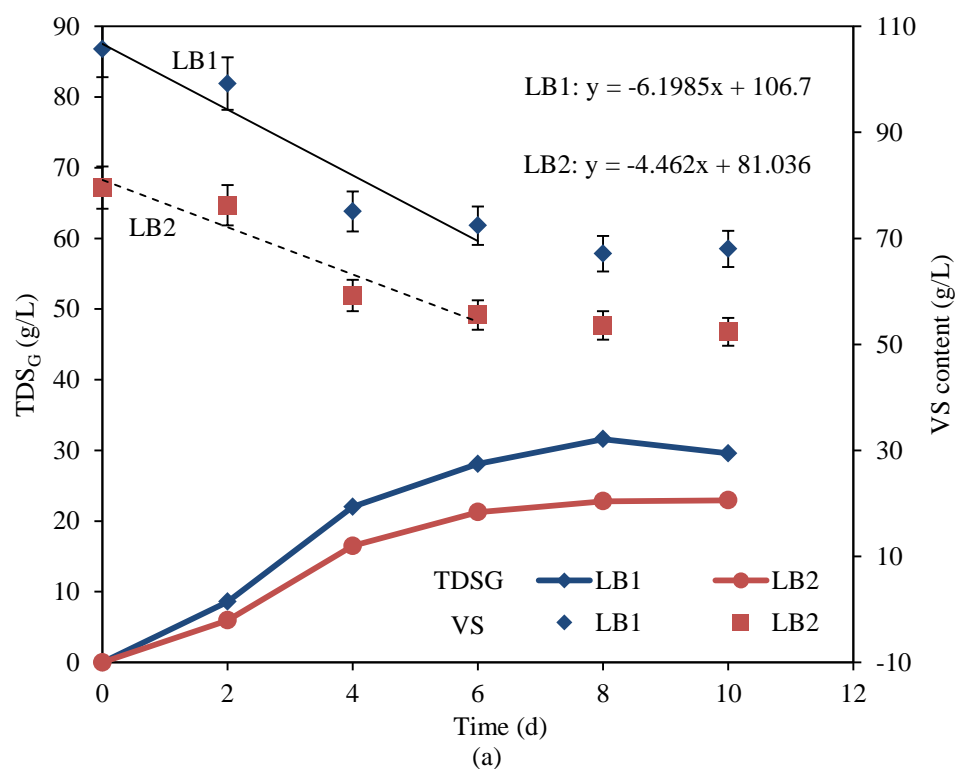


Fig. 3 Time courses for TDS<sub>G</sub> and VS contents

**Fig. 4**

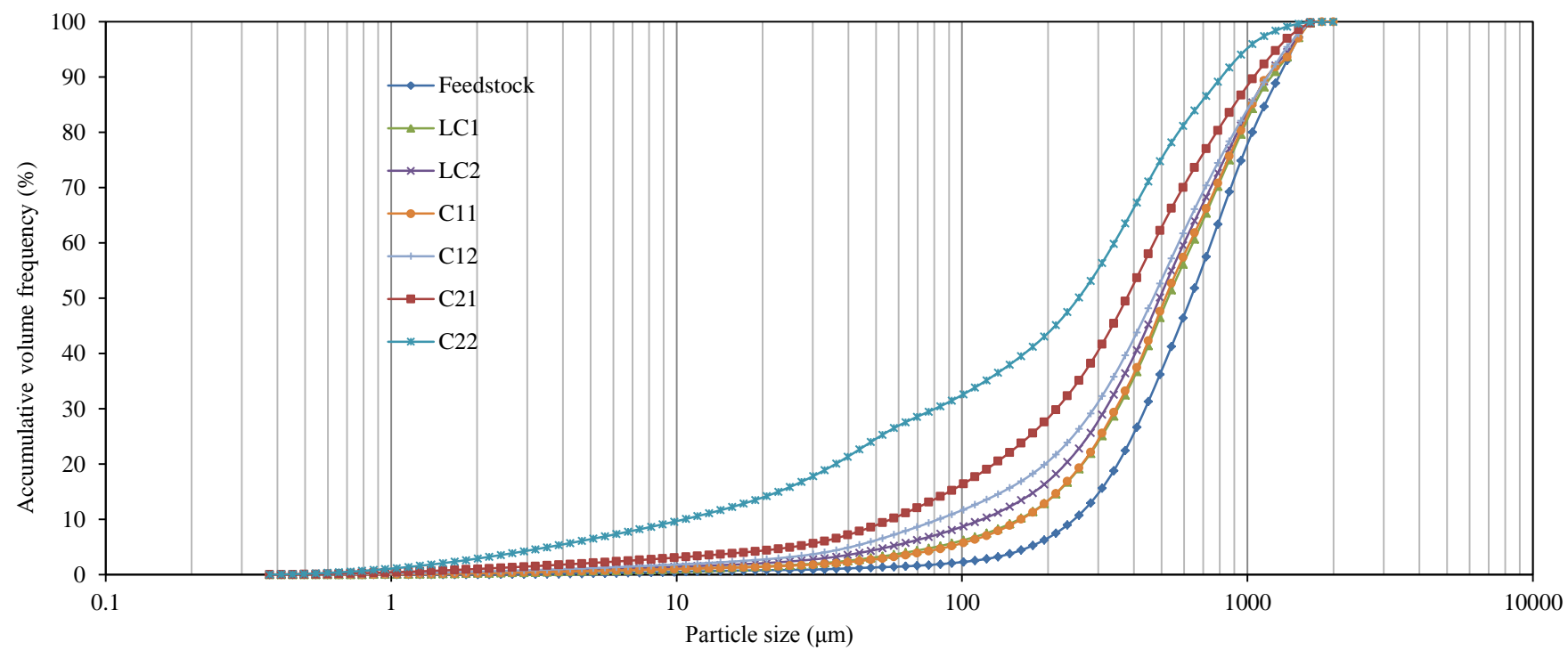


Fig. 4 Particle size distributions in the continuous operations

**Table 1**

Table 1 Operation conditions for the batch operation experiments

Fermentor	Substrate and methanogenic leachate			WRS addition	
	Weight of methanogenic leachate (g)	Weight of Soybean meal (g)	Weight ratio of methanogenic leachate to substrate	Weight (g)	Proportion (in substrate TS, %)
LB1	1200	1200	1:1	0	0
LB2	1600	800	2:1	0	0
B11	1200	1200	1:1	12	5
B12	1200	1200	1:1	24	10
B21	1600	800	2:1	8	5
B22	1600	800	2:1	16	10

**Table 2**

Table 2 Daily operation conditions for the continuous operation experiments

Fermentor	Substrate and methanogenic leachate			WRS addition	
	Weight of methanogenic leachate (g)	Weight of soybean meal (g)	Weight ratio of methanogenic leachate to substrate	Weight (g)	Proportion (in substrate TS, %)
LC1	90	90	1:1	0	0
LC2	120	60	2:1	0	0
C11	90	90	1:1	0.9	5
C12	120	120	1:1	2.4	10
C21	120	60	2:1	0.6	5
C22	140	70	2:1	1.4	10

**Table 3**

Table 3 Pretreatment characteristics of the continuous operations under steady state

	PSD	$K_{sbk}$	$R_{VS}$	$TDS_G$	$S_L$
Fermenter No.	( $\mu m$ )	( $10^{-3} \text{ kg/m}^2 \text{ d}$ )	(%)	(g/L)	-
LC1	662 $\pm$ 12	8.2	17.1	20.8 $\pm$ 0.2	2.02 $\pm$ 0.01
LC2	491 $\pm$ 11	25.4	41.6	42.9 $\pm$ 0.1	2.07 $\pm$ 0.02
C11	656 $\pm$ 9	8.8	11.1	13.6 $\pm$ 0.0	1.99 $\pm$ 0.02
C12	628 $\pm$ 15	11.6	16.2	21.4 $\pm$ 0.1	2.36 $\pm$ 0.03
C21	518 $\pm$ 6	22.6	56.5	45.5 $\pm$ 0.0	2.64 $\pm$ 0.03
C22	351 $\pm$ 15	39.3	68.2	67.0 $\pm$ 0.0	3.02 $\pm$ 0.03



**Table 4**

Table 4 Acidogenesis characteristics of the continuous operations under steady state

Fermenter No.	pH(-)		VA	Apparent $Y_{VA}$	VA distribution		VA spectra (%)			
	In	Out	(g/L)	g-VA/ g-VS	UVA (%)	IVA (%)	Acetic acid	Propionic acid	Butyric acid	Succinic acid
LC1	7.5	5.2	10.9	0.58	26.7	73.3	31.1	20.7	24.6	23.6
LC2	7.5	5.0	10.4	0.23	36.6	63.4	14.6	36.5	26.4	22.5
C11	7.4	5.1	11.7	0.97	31.5	68.5	-	-	-	-
C12	7.5	5.1	10.1	0.73	31.5	68.5	37.9	29.2	25.1	7.8
C21	7.4	5.0	8.9	0.21	36.6	63.4	17.3	58.5	23.1	1.1
C22	7.5	4.9	7.4	0.12	42.1	57.9	9.0	29.3	27.1	34.6

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